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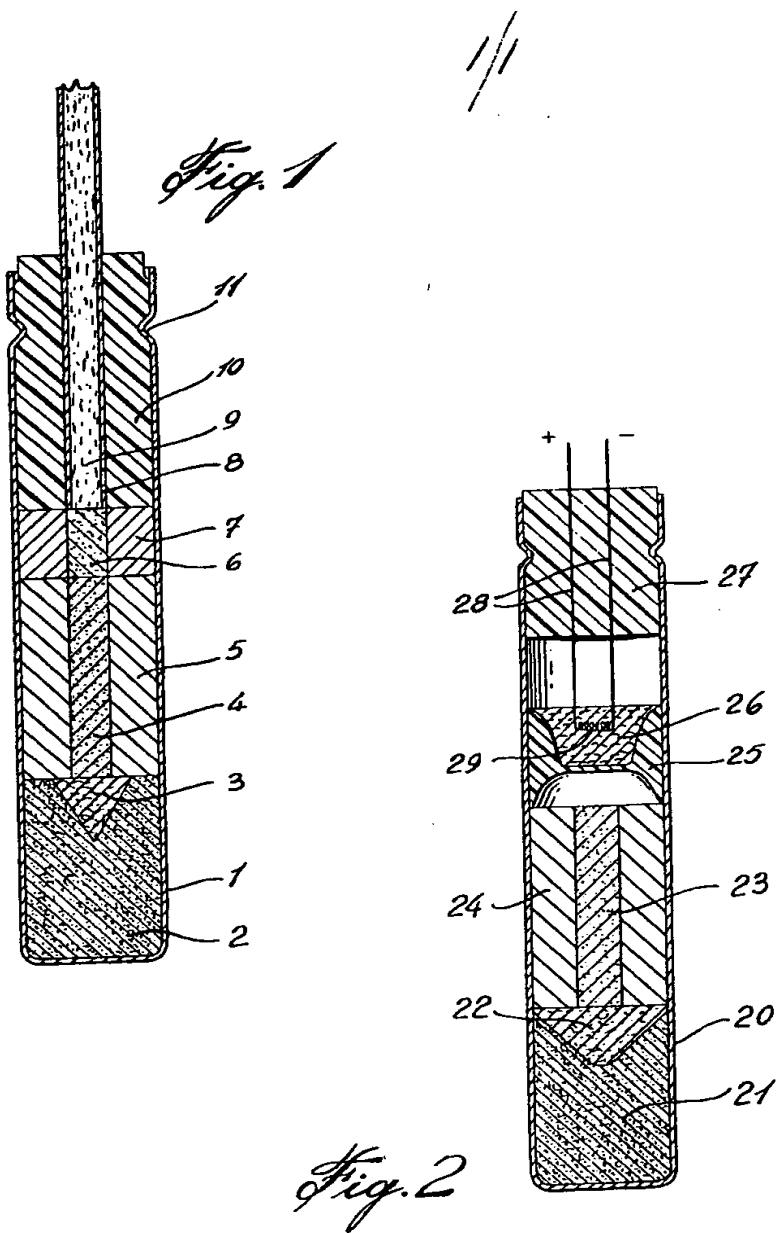
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(57) There is disclosed a pyrotechnic delay composition of intermediate to slow burning time for use in both electric and non-electric blasting caps. The composition comprises a mixture of barium sulphate and silicon to which may optionally be added a proportion of red lead oxide. The composition is characterized by the absence of any recognised carcinogenic properties and is not water soluble.

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## **SPECIFICATION**

## Delay composition for detonators

5 This invention relates to a novel pyrotechnic delay composition characterized by low toxicity, 5  
moisture resistance and uniform burn rate. In particular, the invention relates to a delay  
composition of intermediate to slow-burning time range for use in both non-electric and electric  
blasting caps.

10 Delay detonators, both non-electric and electric, are widely employed in mining, quarrying  
and other blasting operations in order to permit sequential initiation of the explosive charges in a 10  
pattern of boreholes. Delay or sequential initiation of shotholes is effective in controlling the  
fragmentation and throw of the rock being blasted and, in addition, provides a reduction in  
ground vibration and in air blast noise.

15 Modern commercial delay detonators, whether non-electric or electric, comprise a metallic  
shell closed at one end which shell contains in sequence from the closed end a base charge of a  
detonating high explosive, such as for example, PETN and an above adjacent, primer charge of  
a heat-sensitive detonable material, such as for example, lead azide. Adjacent the heat-sensitive  
material is an amount of a deflagrating or burning composition of sufficient quantity to provide a  
desired delay time in the manner of a fuse. Above the delay composition is an ignition charge  
20 adapted to be ignited by an electrically heated bridge wire or, alternatively, by the heat and  
flame of a low energy detonating cord or shock wave conductor retained in the open end of the  
metallic shell.

25 A large number of burning delay compositions comprising mixtures of fuels and oxidizers are  
known in the art. Many are substantially gasless compositions; that is, they burn without  
25 evolving large amounts of gaseous by-products which would interfere with the functioning of the  
delay detonator. In addition to an essential gasless requirement, delay compositions are also  
required to be safe to handle, from both an explosive and health viewpoint, they must be  
resistant to moisture and not deteriorate over periods of storage and hence change in burning  
characteristics, they must be simply compounded and economical to manufacture and they must  
30 be adaptable for use in a wide range of delay units within the limitations of space available  
inside a standard detonator shell. The numerous delay compositions of the prior art have met  
with varying degrees of success in use and application. Some of the prior art compositions  
contain ingredients which are recognized as carcinogenic. Other compositions contain ingredi-  
ents which are soluble in water which may lead to deterioration of the composition in a moist  
35 environment. For example, one widely known delay composition comprising a mixture of  
powdered tungsten metal, particulate potassium perchlorate and barium chromate and diatomaceous  
earth, contains both water soluble material (potassium perchlorate) and a carcinogen  
(barium chromate). Another known type of delay composition consists of a mixture of antimony  
and potassium permanganate or a mixture of zinc, antimony and potassium permanganate.  
40 These compositions, because they contain a water-soluble salt oxidizer, tend to deteriorate in  
hot, moist storage or use environments. As a result, detonators containing such water-soluble  
materials must be constructed to positively exclude any moist atmosphere thus imposing  
problems in manufacture.

45 The present invention provides a pyrotechnic delay composition of intermediate to slow  
burning time which composition contains no recognized carcinogen or any water-soluble  
material. By "intermediate to slow burning time" is meant a burning time of from about 400 to  
about 3200 milliseconds per centimeter of length.

50 In accordance with the invention, an improved pyrotechnic delay composition is provided for  
use in a delay blasting cap assembly which comprises from 45 to 70% by weight of barium  
sulphate and from 30 to 55% by weight of silicon.

55 The barium sulphate/silicon delay composition of the invention may in some cases,  
advantageously contain a proportion of red lead oxide. The inclusion of red lead oxide has the  
effect of somewhat speeding up the burning time of the composition without any adverse effect  
on either toxicity or water solubility. Typically, such a three-component composition comprises  
from 15 to 60% by weight of barium sulphate, from 25 to 75% by weight of red lead oxide  
55 and from 5 to 40% by weight of silicon. While the two-component delay composition of the  
invention comprising barium sulphate/silicon mixture provides a burning time of from about  
1300 to 3200 milliseconds per centimeter of length, the three-component barium sulphate/sili-  
con/red lead oxide mixture provides a somewhat higher burn rate of from about 400 to 2750  
60 milliseconds per centimeter of length.

65 The invention may be more clearly understood by reference to the accompanying drawing  
which illustrates in  
Figure 1 a non-electric delay detonator and in  
Figure 2, an electric delay detonator, showing the position therein of the delay composition of  
65 the invention.

With reference to Fig. 1, 1 designates a metal tubular shell closed at its bottom end and having a base charge of explosive 2 pressed or cast therein. 3 represents a primer charge of heat-sensitive explosive. The delay charge or composition of the invention is shown at 4 contained in drawn lead tube or carrier 5. Surmounting delay charge 4 is ignition charge 6 contained in carrier 7. Above ignition charge 6 is the end of a length of inserted low energy detonating cord 8 containing explosive core 9. Detonating cord 8 is held centrally and securely in tube 1 by means of closure plug 10 and crimp 11. When detonating cord 8 is set off at its remote end (not shown) heat and flame ignites ignition charge 6, in turn, igniting delay composition 4. Composition 4 burns down to detonate primer 3 and base charge 2. 5

10 With reference to Fig. 2, a tubular metal shell 20 closed at its bottom end is shown containing a base charge of explosive 21. A primer charge 22 is indented into the upper surface of charge 21. Above charge 21 and primer 22 and in contact therewith is delay composition 23 contained within a swaged and drawn lead tube or carrier 24. Spaced above delay charge 23 is a plastic cup 25 containing an ignition material charge 26, for example, a red lead/boron mixture. The upper end of shell 20 is closed by means of plug 27 through which pass lead wires 28 joined at their lower ends by resistance wire 29 which is embedded in ignition charge 26. When current is applied to wire 29 through leads 28, charge 26 is ignited. Flame from ignited charge 26 ignites delay composition 23 which in turn sets off primer 22 and explosive 21. 15

20 The invention is illustrated with reference to several series of tests summarized in the following Examples and Tables. 20

#### EXAMPLES 1-8

A number of delay compositions were made by intimately mixing together different proportions of barium sulphate and powdered silicon. The specific surface area of barium sulphate was 0.81 m<sup>2</sup>/g while the specific surface area of silicon was 8.40 m<sup>2</sup>/g. The mixtures were prepared by vigorous mechanical stirring of the ingredients in slurry form utilizing water as the liquid vehicle. After mixing, the slurry was filtered under vacuum and the resulting filter cake was dried and sieved to yield a reasonably free-flowing powder. Delay elements were made by loading lead tubes with these compositions, drawing these tubes through a series of dies to a final diameter of about 6.5 mm and cutting the resultant rod into elements of length 25.4 mm. The delay times of these elements, when assembled into non-electric detonators initiated by NONEL (Reg. TM) shock wave conductor, were measured. Delay time data are given in Table I below while the sensitivities of some of these compositions to friction, impact and electrostatic discharge are shown in Table II below. 35

TABLE I

40	Example	Composition BaSO <sub>4</sub> :Si <sup>1)</sup>	Length of Delay Element (mm)	Number of Detonators Tested	40
1		70:30	25.4	20 <sup>2)</sup>	
2		64:36	25.4	20 <sup>2)</sup>	
45	3	62:38	25.4	20 <sup>2)</sup>	45
4		60:40	25.4	20 <sup>2)</sup>	
5		58:42	25.4	20 <sup>2)</sup>	
6		56:44	25.4	20 <sup>2)</sup>	
7		50:50	25.4	20 <sup>3)</sup>	
50	8	45:55	25.4	20 <sup>2)</sup>	50

TABLE I Cont'd

5	Delay Time (milliseconds)					5
	Example	Mean	Min.	Max.	Scatter	
10 1	3385	3224	3541	317	2.40	10
2	5062	4834	5184	350	1.77	
3	5325	5172	5476	304	1.71	
4	5681	5527	5786	259	1.36	
5	5936	5839	6003	164	0.66	
15 6	5642	5529	5765	236	0.98	15
7	5089	4966	5360	394	1.95	
8	4466	4256	4856	600	2.99	

## Notes:

20 1) BaSO<sub>4</sub> specific surface area 0.81 m<sup>2</sup>/g; Si specific surface area 8.40 m<sup>2</sup>/g.  
 2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 95 milliseconds.  
 3) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon-Ottawa sand (SiO<sub>2</sub>) igniter element. Delay times quoted above include delay time contribution of these two igniter elements, nominally 160 milliseconds.  
 4) Delay time coefficient of variation is delay time standard deviation expressed as a percentage of mean delay time.

30

TABLE II

35	Composition BaSO <sub>4</sub> :Si <sup>1)</sup>	Impact <sup>2)</sup>	Friction <sup>3)</sup>	Electrostatic Discharge <sup>4)</sup>	35
		Min. Ignition Height (cm)	Min. Ignition Height (cm)	Min. Ignition Energy (mJ)	
40	70:30	>139.7	>83.8	>256.5	40
	65:35	>139.7	>83.8	>256.5	
	60:40	>139.7	>83.8	>256.5	
	55:45	>139.7	>83.8	>256.5	45
45	50:50	>139.7	>83.8	>256.5	
	45:55	>139.7	>83.8	>256.5	

## Notes:

50 1) BaSO<sub>4</sub> specific surface area 0.81 m<sup>2</sup>/g; Si specific surface area 8.40 m<sup>2</sup>/g.  
 2) In impact test, mass of fall-hammer (steel) 5.0 kg. Samples tested in copper/zinc (90/10) cup.  
 3) In friction test, mass of torpedo (with aluminum head) 2.898 kg. Samples tested on aluminum blocks.  
 4) Discharge from 570 pF capacitor.

55 EXAMPLE 9  
 The relationship between means delay time and length of delay element was established for a barium sulphate-silicon 58:42 composition. Again, the tests were performed using non-electric detonators initiated by NONEL (Reg. TM). Results are shown in Table III below.

TABLE III

5 Example	Composition BaSO <sub>4</sub> :Si <sup>1)</sup>	Length (L) of Delay Element (mm)	Number of Detonators Tested	5
9	58:42)	6.35	20 <sup>2)</sup>	
	)	12.7	20 <sup>2)</sup>	
10	)	25.4	20 <sup>2)</sup>	10

TABLE III Cont'd

15	Delay Time (milliseconds)				Relation between Mean Delay Time (T) and Delay Element Length (L)	15
20	Mean	Min.	Max.	Scatter	Coefficient of Variation (%)	20
1449	1381	1515	134	2.26	( T = 234.7 L -	
3022	2934	3104	170	1.24	( 8.0 ms	
5936	5839	6003	164	0.66	( (Correlation coefficient ( 0.9998)	25

## Notes:

1) BaSO<sub>4</sub> specific surface area 0.81 m<sup>2</sup>/g; Si specific surface area 8.40 m<sup>2</sup>/g.  
 2) Each detonator incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 95 milliseconds.

From the results shown in Table III, it can be seen that a strong linear relationship exists between mean delay time and length of barium sulphate-silicon delay element. This characteristic is important in manufacturing processes that utilize drawn lead delay elements, as it affords control of nominal delay times by simple manipulation of element cutting lengths.

## EXAMPLE 10

A evaluation of the low-temperature timing performance of barium sulphate-silicon compositions was made by subjecting non-electric detonators containing a BaSO<sub>4</sub>:Si 58:42 pyrotechnic mixture to a temperature of - 45°C for a period of 24 hours. The detonators were subsequently fired at that temperature by means of NONEL (Reg. TM) shock wave conductor and their delay times were noted. Timing results are given in Table IV below.

45

TABLE IV

50 Example	Composition BaSO <sub>4</sub> :Si <sup>1)</sup>	Test Temperature (°C)	Number of Detonators Tested/Number Fired	50
10	58.42	20	20/20 <sup>2)</sup>	
	58:42	- 45	15/15 <sup>2)</sup>	

TABLE IV Cont'd

Delay Time (milliseconds)					% Change in Delay Time (20°C to -45°C)	% Change in Delay Time/°C	5
	Mean	Min.	Max.	Scatter	Coefficient of Variation (%)		10
10	3022	2934	3104	170	1.24	3.84	
	3138	3068	3218	150	1.48	0.059	10

**Notes:**1) BaSO<sub>4</sub> specific surface area 0.81 m<sup>2</sup>/g; Si specific surface area 8.40 m<sup>2</sup>/g.15 2) Each detonator had a 12.7 mm long red lead-silicon igniter element, a 6.35 mm long red lead-silicon igniter element and a 6.35 mm long barium sulphate-silicon delay element. Delay times quoted include delay time contributions of igniter elements, nominally 95 milliseconds. As seen from the results in Table IV, the temperature coefficient of the BaSO<sub>4</sub>:Si 58:42 composition over the temperature range -45°C to +20°C is 0.059 percent per degree C.

20 Also, it can be noted that no failure occurred in these low-temperature firing tests.

**EXAMPLE 11**

In order to assess the effect of the specific surface area of silicon on the delay time characteristics of barium sulphate-silicon composition, three mixtures, each consisting of BaSO<sub>4</sub>-Si in the mass ratio 58:42, were prepared. Silicon samples of specific surface area 8.40, 7.20 and 6.05 m<sup>2</sup>/g were used in the preparation of the compositions under test. The delay times of these compositions were measured in assembled NONEL (Reg. TM) initiated non-electric detonators. The results which were obtained are summarized in Table V, below, where it can be seen that as the fuel specific surface area is decreased the greater is the delay time of the composition.

TABLE V

35	Example	Composition BaSO <sub>4</sub> :Si <sup>1)</sup>	Specific Surface Area of Silicon (m <sup>2</sup> /g)	Length of Delay Element (mm)	Number of Detonators Tested	35
40	11	58:42	8.40	25.4	20 <sup>2)</sup>	
		58.42	7.20	25.4	20 <sup>2)</sup>	40
		58.42	6.05	25.4	20 <sup>2)</sup>	

45 TABLE V Cont'd

Delay Time (milliseconds)					50	
	Mean	Min.	Max.	Scatter	Coefficient of Variation (%)	50
55	5936	5839	6003	164	0.66	
	6603	6453	6749	296	1.26	
	8065	7495	8351	856	2.61	55

**Notes:**1) BaSO<sub>4</sub> specific surface area 0.81 m<sup>2</sup>/g.

2) Each detonator incorporated a 12.7 mm red lead-silicon igniter element and a 6.35 mm red lead-silicon igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 95 milliseconds.

**EXAMPLE 12**

The suitability for use in electric detonators of one of the compositions of the invention was determined. The oxidant-fuel combination which was evaluated was 60:40 BaSO<sub>4</sub>-Si by mass.

65 Barium sulphate of specific surface area 0.81 m<sup>2</sup>/g and silicon of specific surface area 8.40

$\text{m}^2/\text{g}$  were employed. Electric detonators, each having a delay train consisting of a 6.35 mm long red lead-silicon-Ottawa sand ( $\text{SiO}_2$ ) igniter element superimposed on a 25.4 mm long barium sulphate-silicon delay element, were assembled and fired. Statistical data on the timing performance of these detonators is condensed in Table VI. Included in Table VI, for comparison, are the corresponding timing results obtained for the same mixture in non-electric, NONEL (Reg. TM) initiated detonators. 5

TABLE VI

10	Example	Composition $\text{BaSO}_4:\text{Si}^{11}$	Detonator Type	Length of Delay Ele- ment (mm)	Number of Detonators Tested	10
12	60:40	Non-electric		25.4	20 <sup>21</sup>	
15	60:40	Electric		25.4	20 <sup>31</sup>	15

TABLE VI Cont'd

20	Delay Time (milliseconds)					20
25	Mean	Min.	Max.	Scatter	Coefficient of Variation (%)	25
5681	5527	5786	259		1.36	
5075	4905	5173	268		1.33	

*Notes:*

30 1)  $\text{BaSO}_4$  specific surface area  $0.81 \text{ m}^2/\text{g}$ ; Si specific surface area  $8.40 \text{ m}^2/\text{g}$ .  
 2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 95 milliseconds.  
 3) Denotes detonators which incorporated a 6.35 mm long red lead-silicon-Ottawa sand ( $\text{SiO}_2$ ) igniter element. Delay times quoted include delay time contribution of this igniter element, nominally 85 milliseconds.

**EXAMPLES 13-19**

A series of seven delay compositions comprising barium sulphate/red lead oxide/silicon mixtures were compounded in which the silicon proportion was varied from 5.7 percent to 35.0 percent by weight of the total composition while the ratio of oxidants barium sulphate/red lead oxide was held constant at 0.80. The effect of these formulation changes on composition delay time was measured. In the formulations the specific surface area of silicon was  $1.79 \text{ m}^2/\text{g}$ ; barium sulphate and red lead oxide had specific surface areas of  $0.81 \text{ m}^2/\text{g}$  and  $0.73 \text{ m}^2/\text{g}$  respectively. The mixtures were prepared by vigorous mechanical stirring of the ingredients in slurry form utilizing water as the liquid vehicle. After mixing, the slurry was filtered under vacuum and the resulting filter cake was dried and sieved to yield a reasonably free-flowing powder. Delay elements were made by loading lead tubes with the compositions, drawing the lead tubes through a series of dies of decreasing diameter to a final diameter of about 6.5 mm, and cutting the resultant rod into elements. Non-electric detonators initiated by means of NONEL (Reg. TM) shock wave conductor were loaded with the delay elements, fired and the delay times noted. A summary of the delay times is given in Table VII, below.

TABLE VII

5	Example	Composition		Length of delay element (mm)	Number of detonators fired	5
	13	BaSO <sub>4</sub> :	52.4: 5.7	25.4	20 <sup>2)</sup>	
	14	41.5:	51.8: 6.7	25.4	20 <sup>2)</sup>	
10	15	40.0:	50.0:10.0	25.4	20 <sup>3)</sup>	10
	16	37.8:	47.2:15.0	25.4	20 <sup>3)</sup>	
	17	35.6:	44.4:20.0	25.4	20 <sup>3)</sup>	
	18	31.1:	38.9:30.0	25.4	20 <sup>3)</sup>	
	19	28.9:	36.1:35.0	25.4	20 <sup>3)</sup>	
15						15

TABLE VII Cont'd

20	Delay time (milliseconds)					20	
	Example	Mean	Min.	Max.	Scatter	Coefficient of variation (%)	
25	13	7034	6867	7318	451	1.56	25
	14	5324	5186	5423	237	1.19	
	15	1779	1739	1815	76	1.18	
	16	1106	1078	1148	70	1.63	
30	17	1365	1324	1418	94	1.83	30
	18	2541	2492	2593	101	1.13	
	19	4155	4010	4348	338	1.75	

## Notes:

1) Silicon of specific surface area 1.79 m<sup>2</sup>/g  
 35 2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 95 milliseconds.  
 30 3) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon-Ottawa sand (SiO<sub>2</sub>) igniter element. Delay times quoted above include delay time contribution of these two igniter elements, nominally 160 milliseconds.

## EXAMPLES 20-27

In a series of eight tests, formulations comprising barium sulphate/red lead oxide/silicon mixtures were compounded in the same manner as described in Examples 13-19 in which the silicon proportion was held constant at 6.7 percent by weight while the ratio of oxidants barium sulphate/red lead oxide was varied from 0.26 to 0.90. Again, the specific surface areas of barium sulphate, red lead oxide and silicon were 0.81, 0.73 and 1.79 m<sup>2</sup>/g respectively. The delay time characteristics of the compositions, tested in non-electric NONEL initiated detonators, 50 are shown in Table VIII. It should be noted that a control sample of composition containing no barium sulphate was included in these tests. The performance of this control sample, consisting of Pb<sub>3</sub>O<sub>4</sub>/Si in the ratio 93.3:6.7, is also shown in Table VIII.

The data shown in Table VIII demonstrates that in the case of BaSO<sub>4</sub>/Pb<sub>3</sub>O<sub>4</sub>/Si compositions in which the proportion of silicon is fixed, any increase in the proportion of barium sulphate (at the expense of red lead oxide) has the effect of retarding the delay time of the composition.

55

TABLE VIII

5	Example	Composition			Length of delay element (mm)	Number of detonators fired	5
		BaSO <sub>4</sub> :	Pb <sub>3</sub> O <sub>4</sub> :	Si <sup>1)</sup>			
20	20	44.2:	49.1:	6.7	25.4	10 <sup>2)</sup>	
21	21	42.2:	51.1:	6.7	25.4	10 <sup>2)</sup>	
10 22	22	40.7:	52.6:	6.7	25.4	20 <sup>3)</sup>	10
23	23	37.2:	56.1:	6.7	25.4	20 <sup>3)</sup>	
24	24	34.2:	59.1:	6.7	25.4	20 <sup>3)</sup>	
25	25	29.2:	64.1:	6.7	25.4	20 <sup>3)</sup>	
26	26	24.2:	69.1:	6.7	25.4	20 <sup>3)</sup>	
15 27	27	19.2:	74.1:	6.7	25.4	20 <sup>3)</sup>	15
—	—	nil:	93.3:	6.7	25.4	20 <sup>3)</sup>	

20 TABLE VIII cont'd 20

Delay time (milliseconds)						25	
25	Example	Mean	Min.	Max.	Scatter	Coefficients of variation (%)	25
20	20	7454	7329	7565	236	0.99	
21	21	6114	6019	6290	271	1.19	
22	22	4941	4894	4988	94	0.50	
30 23	23	2844	2773	2916	143	1.59	30
24	24	2132	2096	2169	73	0.82	
25	25	1642	1621	1658	37	0.56	
26	26	1393	1380	1416	36	0.62	
27	27	1202	1190	1211	21	0.45	
35	—	449	406	473	67	4.60	35

## Notes:

1) Specific surface area of silicon 1.79 m<sup>2</sup>/g

2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element

40 and a 6.35 mm long red lead-silicon-Ottawa sand (SiO<sub>2</sub>) igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 160 milliseconds.

3) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 95 milliseconds.

45 EXAMPLE 28 45

The effect of the specific surface area of silicon on the mean delay time of barium sulphate-red lead oxide-silicon composition was assessed. The formulation selected was BaSO<sub>4</sub>/Pb<sub>3</sub>O<sub>4</sub>/Si in the ratio 44.2:49.1:6.7 respectively by weight. Silicon samples of specific surface areas 50 1.79, 3.71 and 8.40 m<sup>2</sup>/g were used to make the compositions under test. The results which were obtained are condensed in Table IX, where it can be seen that the mean delay time decreases as silicon specific surface area is increased.

55	Example	Composition			Specific Surface Area of Silicon	Length of Delay Element (mm)	55
		BaSO <sub>4</sub> :	Pb <sub>3</sub> O <sub>4</sub> :	Si			
60	)	44.2:	49.1:	6.7	1.79	25.4	
28)		44.2:	49.1:	6.7	3.71	25.4	
)		44.2:	49.1:	6.7	8.40	25.4	60

TABLE IX Cont'd

5	Example	Number of Detonators Fired	Delay time (milliseconds)				5
			Mean	Min.	Max.	Scatter	
10	)	10 <sup>1)</sup>	7454	7329	7565	236	0.99
28)	)	20 <sup>2)</sup>	1535	1492	1568	76	1.24
	)	20 <sup>2)</sup>	753	746	761	15	0.55

## Notes:

15 1) Denotes detonators which incorporated 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon-Ottawa sand ( $\text{SiO}_2$ ) igniter element. Delay times quoted include delay time contribution of these igniter elements, nominally 160 milliseconds.

2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of these igniter elements, nominally 95 milliseconds.

## EXAMPLES 29 &amp; 30

The relationships between mean delay time and delay element length were determined for two of the compositions of the invention namely  $\text{BaSO}_4/\text{Pb}_3\text{O}_4/\text{Si}$  in the ratio 29.2:64.1:6.7 and 25 also in the ratio 41.5:51.8:6.7 by weight. Lead-drawn delay elements of lengths 6.35, 12.7, 25.4 and 50.8 mm made with these compositions were assembled into non-electric, NONEL (Reg. TM) initiated detonators, subsequently fired and the delay times noted. Results are shown in Table X. From these results it can be seen that, for the two formulations tested, strong linear relationships exist between mean delay time and delay element length. This characteristic is 30 important in manufacturing processes which utilize lead-drawn delay elements, as it affords control of nominal delay times by simple manipulation of element cutting lengths.

TABLE X

35	Example	Composition			Length of (L) Delay Element (mm)	Number of Detonators Fired	35
		$\text{BaSO}_4:$	$\text{Pb}_3\text{O}_4:$	Si <sup>1)</sup>			
40	29	29.2:	64.1:	6.7)	6.35	20 <sup>2)</sup>	40
		)	)	)	12.7	20 <sup>2)</sup>	
		)	)	)	25.4	20 <sup>2)</sup>	
		)	)	)	50.8	20 <sup>2)</sup>	
45	30	41.5:	51.8:	6.7)	6.35	20 <sup>3)</sup>	45
		)	)	)	12.7	20 <sup>3)</sup>	
		)	)	)	25.4	20 <sup>3)</sup>	
		)	)	)	50.8	20 <sup>3)</sup>	

TABLE X Cont'd

5	Delay time (milliseconds)					Relation Between Mean Delay Time (T) & Length (L) of Delay Element	5	
	Example	Mean	Min.	Max.	Scatter	Coefficient of Variation %		
10 29	478 859 1646 3237	452 844 1629 3204	502 870 1660 3267	50 26 31 63	2.64 ) 0.72 ) 0.57 ) 0.58 )	T(ms) = 62.17 (L) + 74.4 ms (Correlation co- efficient 0.9999)	10	
15 30	1134 2602 5392 10317	1074 2402 5178 9896	1243 2690 5506 10490	169 288 328 594	3.51 ) 2.75 ) 1.57 ) 1.49 )	T(ms) = 205.5 (L) - 33.1 ms (Correlation co- efficient 0.9993)	15	
20	Notes:							20
	1) Specific surface area of silicon 1.79 m <sup>2</sup> /g 2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of this igniter element, nominally 70 milliseconds.							25
	3) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon-Ottawa sand (SiO <sub>2</sub> ) igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 160 milliseconds.							25
30	<b>EXAMPLES 31 and 32</b> An assessment of the low temperature timing performance and reliability of the BaSO <sub>4</sub> / Pb <sub>3</sub> O <sub>4</sub> /Si compositions of the invention was made by subjecting non-electric detonators containing two of the above mentioned pyrotechnic mixtures to a temperature of -45°C for a period of 24 hours. The detonators were subsequently fired at that temperature by means of 35 NONEL (Reg. TM) shock wave conductor and their delay times were noted. Results are given in Table XI. It can be noted that no failure occurred in these low temperature firing tests.							30
35								35

TABLE XI

40	Example	Composition			Length of Delay Element (mm)	Test temp. (°C)	Number of Detonators Fired & Tested	40
		BaSO <sub>4</sub> :	Pb <sub>3</sub> O <sub>4</sub> :	Si <sup>1)</sup>				
45	31	29.2:	64.1:	6.7)	25.4	20	20 <sup>2)</sup> /20 <sup>2)</sup>	
	32	41.5:	51.8:	6.7)	25.4	-45	20 <sup>2)</sup> /20 <sup>2)</sup>	45
				)	25.4	20	20 <sup>3)</sup> /20 <sup>3)</sup>	
						-45	20 <sup>3)</sup> /20 <sup>3)</sup>	

50	TABLE XI Cont'd							50
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55	Example	Delay time (milliseconds)					55
		Mean	Min.	Max.	Scatter	Coefficient of Variation (%)	
60	31	1646 1836	1629 1800	1660 1875	31 75	0.57 ) 1.10 )	
	32	5392 7123	5178 6752	5506 7319	328 567	1.57 ) 2.11 )	60

TABLE XI Cont'd

5	Example	% Change in Delay time (20°C to -45°C)	% Change in Delay time/°C	5
31		11.54	0.178	
32		32.10	0.494	10

10 **Notes:**

- 1) Specific surface area of silicon 1.79 m<sup>2</sup>/g
- 2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of this igniter element, nominally 70 milliseconds.
- 3) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element and a 6.35 mm long red lead-silicon-Ottawa sand (SiO<sub>2</sub>) igniter element. Delay times quoted include delay time contribution of these two igniter elements, nominally 160 milliseconds.

15 20 **EXAMPLE 33**

In order to demonstrate the suitability of the composition of the present invention for use in electric detonators, the timing performance in electric detonators of a mixture of BaSO<sub>4</sub>/Pb<sub>3</sub>O<sub>4</sub>/Si in the weight ratio 29.2:64.1:6.7 was determined. Results are shown in Table XII. Included in Table XII for comparison, are the corresponding timing results obtained for the same 25 mixture in non-electric, NONEL (Reg. TM) initiated detonators.

TABLE XII

30	Example	Composition			Detonator Type	Length of Element (mm)	Number of Detonators Tested	30
35	33 )	29.2:	64.1:	6.7	Non-electric	25.4	20 <sup>2)</sup>	35
35	33 )	29.2:	64.1:	6.7	Electric	25.4	10 <sup>3)</sup>	

40 40 **TABLE XII Cont'd**

45	Example	Delay time (milliseconds)					45
		Mean	Min.	Max.	Scatter	Coefficient of Variation (%)	
33 )	1642	1621	1658	37	0.56		
33 )	1559	1528	1584	56	1.07		

50 50 **Notes:**

- 1) Specific surface area of silicon 1.79 m<sup>2</sup>/g
- 2) Denotes detonators which incorporated a 12.7 mm long red lead-silicon igniter element. Delay times quoted include delay time contribution of this igniter element, nominally 70 milliseconds.

55 55 3) No igniter element was used in electric detonators.

The components of the novel delay composition of the invention must be in a finely divided state to insure intimate contact between the oxidants and fuel. Measured in terms of specific surface area, the barium sulphate ranges from 0.5 to 3.0 m<sup>2</sup>/g, preferably 0.8 to 2.7 m<sup>2</sup>/g, the red lead oxide ranges from 0.3 to 1.0 m<sup>2</sup>/g, preferably from 0.5 to 0.8 m<sup>2</sup>/g, and the silicon ranges from 1.4 to 10.1 m<sup>2</sup>/g, preferably from 1.8 to 8.5 m<sup>2</sup>/g. The oxidizers and fuel may advantageously be slurried with vigorous stirring in water as a carrier, the water removed by vacuum filtration and the filter cake dried and sieved to yield a free-flowing, fine powder ready for use.

## CLAIMS

1. A pyrotechnic delay composition adapted for non-electric and electric delay detonators comprising from 45% to 70% by weight of particulate barium sulphate and from 30% to 55% by weight of particulate silicon. 5
2. A pyrotechnic delay composition as claimed in Claim 1 also containing from 25% to 75% by weight of particulate red lead oxide. 5
3. A pyrotechnic delay composition as claimed in Claim 3 comprising from 15% to 60% by weight of particulate barium sulphate, from 5% to 40% by weight of particulate silicon and from 25% to 75% by weight of particulate red lead oxide. 10
4. A pyrotechnic delay composition substantially as hereinbefore described in any one of the foregoing examples. 10
5. A delay blasting detonator having a delay composition as claimed in any one of the preceding claims interposed between an ignition element and a primer/detonation element. 15
6. A delay blasting detonator substantially as hereinbefore described in any one of the foregoing examples. 15

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